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Synthesis and X-ray structure of the heteronuclear cluster, $(\mu\text{-H})_2(\eta^5\text{-C}_5H_5)IrOs_3(CO)_{10}$

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Abstract

$(\mu\text{-H})_2(\eta^5\text{-C}_5H_5)IrOs_3(CO)_{10}$ was prepared in 21% yield by reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with $(\eta^5\text{-C}_5H_5)Ir(CO)_2$. The cluster was characterized by IR, ^1H and ^{13}C NMR, and mass spectrometry and by X-ray crystallography. The structure of $(\mu\text{-H})_2(\eta^5\text{-C}_5H_5)IrOs_3(CO)_{10}$ consists of a tetrahedral cluster core with a semi-bridging carbonyl from Ir to Os. It closely resembles the other members of the series $(\mu\text{-H})_2(\eta^5\text{-C}_5H_5)MOs_3(CO)_{10}$ (M = Co, Rh). The semi-bridging carbonyl has greater bridging character as M = Ir < Rh < Co. This is reflected in the relative intensities and shapes of the semi-bridging CO stretching bands in the IR spectra and in the ^{13}C NMR chemical shifts of the semi-bridging carbonyl signals of the compounds. The semi-bridging carbonyl ^{13}C resonance is shifted to higher field from cobalt to iridium.

Introduction

The reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with metal carbonyls under conditions (thermal [1–8] or photolytic [9]) that cause formation of unsaturated metal carbonyl fragments has been shown to be a general route to triosmium based mixed-metal clusters [10,11]. Earlier work in this laboratory showed that the presence or absence of added H_2 had a significant effect on the types and distributions of products that were formed [3,5–8]. The reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with $(\eta^5\text{-C}_5H_5)M(CO)_2$ (M = Co, Rh) in the absence of added H_2 resulted in high yields of $(\mu\text{-H})_2(\eta^5\text{-C}_5H_5)CoOs_3(CO)_{10}$ [2] and $(\mu\text{-H})_2(\eta^5\text{-C}_5H_5)RhOs_3(CO)_{10}$ [5,7]. Some systematic studies of trinuclear clusters have been reported in which one of the metals is varied down a group of the periodic table [12], but the tetranuclear clusters have not been examined in this manner. It was of interest to complete the series $(\mu\text{-H})_2(\eta^5\text{-C}_5H_5)MOs_3(CO)_{10}$ (M = Co, Rh, Ir) through the synthesis and structural characterization of the iridium analogue. Reported here are the synthesis and characterization of $(\mu\text{-H})_2(\eta^5\text{-C}_5H_5)IrOs_3(CO)_{10}$. Its structure and spectral properties are discussed and compared with the other members of the series.

Experimental

Chemicals and solvents

Ir(CO)$_3$Cl (Strem), Os$_3$(CO)$_{12}$ (Strem), cyclopentadiene (Aldrich), and ^{13}CO, 99.9% ^{13}C (Matheson Scientific Products) were all used without further purification. Toluene (Aldrich) was dried by means of refluxing and storing over sodium benzophenone ketyl. Hexane was dried by stirring it over concentrated H_2SO_4, then by stirring it over KH and distilling it into a glass storage bulb. (μ-H)$_2$Os$_3$(CO)$_{10}$ [13] was prepared by a published method.

Infrared and NMR spectra

Infrared spectra of solutions were recorded on a Mattson Cygnus-25 FTIR spectrometer. Proton and carbon-13 spectra were obtained on a Bruker-500 spectrometer at 500.14 and 125.76 MHz respectively. Chemical shifts are referred to Si(CH$_3$)$_4$ (^{1}H NMR, δ 0.00 ppm) and Si(^{13}CH$_3$)$_4$ (^{13}C NMR, δ 0.00 ppm).

X-Ray structure determination

A suitable crystal was mounted on the tip of a glass fiber. All X-ray data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (0.710730 Å), and all crystallographic computations were carried out on a PDP 11/44 computer using SDP (Structure Determination Package) [14]. Crystal data are given in Table 1.

Lattice parameters were obtained by a least squares refinement of the angular settings from 25 reflections lying in a 2θ range of 24–30°. Intensity data ($4 < 2\theta < 55°$) were collected in the 2θ scan mode. Intensity data showed no significant decay. Data were corrected for absorption using the numerical method based on the Gaussian integration formula with a grid of 24 × 4 × 14 points [15].

The structure was solved by a combination of the direct method MULTAN 11/82 and the difference Fourier technique, and was refined by full-matrix least squares refinement. Analytical atomic scattering factors were used throughout the struc-

Table 1

Crystal data for (μ-H)$_2$(η^5-C$_5$H$_5$)IrOs$_3$(CO)$_{10}$

Chemical formula	$C_{15}H_7O_{10}Os_3Ir$
Formula weight	1110.02
Space group	*Pbca* (No. 61)
T (°C)	25
a (Å)	15.171(2)
b (Å)	17.756(2)
c (Å)	14.829(2)
V (Å^3)	3994.5
Z	8
λ (Å)	0.71073
$\rho_{calc.}$ (g cm^{-3})	3.691
μ (cm^{-1})	257.23
Transmission coefficient (%)	0.9–10.34
$R(F)$	0.065
$R_w(F)$	0.083

Table 2

Positional parameters and their estimated standard deviations (e.s.d.s) for $(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{IrOs}_3(\text{CO})_{10}$

Atom	x	y	z	B (Å^2) [a]
Ir	0.30800(5)	0.15019(5)	0.04771(5)	2.45(1)
Os1	0.18572(5)	0.23334(4)	0.14157(5)	2.46(1)
Os2	0.14298(5)	0.08264(5)	0.07118(6)	2.59(1)
Os3	0.25956(6)	0.09592(5)	0.21340(5)	2.69(1)
C11	0.163(2)	0.293(2)	0.037(2)	4.3(5)
C12	0.280(2)	0.301(1)	0.182(2)	4.0(5)
C13	0.091(2)	0.279(1)	0.207(2)	4.1(5)
C21	0.175(2)	−0.015(2)	0.032(2)	4.3(5)
C22	−0.054(2)	−0.094(1)	0.022(2)	3.1(4)
C23	0.069(2)	0.042(2)	0.165(2)	4.5(6)
C24	0.220(2)	0.150(1)	−0.043(2)	4.7(5)
C31	0.354(2)	0.134(2)	0.283(1)	3.6(5)
C32	0.319(2)	0.003(1)	0.183(2)	3.9(5)
C33	0.201(2)	0.053(1)	0.311(1)	3.5(4)
O11	0.150(1)	0.323(1)	−0.028(1)	7.0(5)
O12	0.327(1)	0.340(1)	0.207(1)	4.5(4)
O13	0.036(1)	0.309(1)	0.245(1)	5.3(4)
O21	0.194(1)	−0.075(1)	0.010(1)	5.5(5)
O22	0.001(1)	0.106(1)	−0.072(1)	5.2(4)
O23	0.023(1)	0.020(1)	0.215(1)	5.5(4)
O24	0.203(1)	0.152(1)	−0.119(1)	6.2(5)
O31	0.410(2)	0.160(1)	0.326(1)	6.7(5)
O32	0.354(1)	−0.048(1)	0.167(2)	6.1(5)
O33	0.162(2)	0.025(1)	0.367(1)	5.5(5)
C41	0.449(1)	0.121(1)	0.087(7)	4.0(5)
C42	0.435(1)	0.203(2)	0.086(2)	4.6(6)
C43	0.414(2)	0.224(1)	−0.005(2)	5.4(5)
C44	0.413(2)	0.155(2)	−0.055(2)	4.7(6)
C45	0.434(1)	0.095(1)	0.003(2)	4.3(5)
H41	0.49(2)	0.08(2)	0.15(2)	*
H42	0.48(2)	0.24(2)	0.15(2)	*
H43	0.38(2)	0.27(2)	−0.01(2)	*
H44	0.39(2)	0.12(2)	−0.14(2)	*
H45	0.42(2)	0.05(2)	−0.03(2)	*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)\times[a^2\times B(1,1)+b^2\times B(2,2)+c^2\times B(3,3)+ab(\cos\gamma)\times B(1,2)+ac(\cos\beta)\times B(1,3)+bc(\cos\alpha)\times B(2,3)]$.

ture refinement. Full-matrix least squares refinements minimizing $(|F_o|-|F_c|)$ were carried out using anisotropic thermal parameters for all non-hydrogen atoms. Weights were taken as $w=[\sigma(I)^2+(kI)^2]^{-1/2}$. Final positional parameters are given in Table 2.

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Ir(CO)}_2$

$(\eta^5\text{-C}_5\text{H}_5)\text{Ir(CO)}_2$ was prepared following a published procedure [16] with slight modifications, by reaction of $\text{Ir(CO)}_3\text{Cl}$ (0.510 g, 1.6 mmol) with $\text{K(C}_5\text{H}_5)$ (3.7 g, 35 mmol) in 40 mL of hexanes at 40°C for 12 h. This gave a brown solid and a yellow solution which was filtered *in vacuo*. The solution was cooled to 0°C and the solvent removed by evaporation into a −196°C trap under static vacuum. This gave a yellow liquid, $(\mu^5\text{-}C_5H_5)Ir(CO)_2$ (0.426 g, 1.35 mmol, 85% yield based on $Ir(CO)_3Cl$), which was characterized by IR and ^{1}H NMR spectroscopy [16].

Preparation of ^{13}CO enriched $(\mu\text{-}H)_2(\eta^5\text{-}C_5H_5)IrOs_3(CO)_{10}$

Freshly prepared $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ (188 mg, 0.60 mmol) was added to a 100-mL flask containing $(\mu\text{-}H)_2Os_3(CO)_{10}$ (170 mg, 0.20 mmol, ~25% ^{13}CO enriched [17]) in 40 mL of dried toluene. The solution was stirred at 90°C for 12 days. Volatiles were removed by means of rotary evaporation leaving a brown solid in the flask. The products were separated by TLC on silica (2 mm) using toluene/heptane (1:4) as eluent. This yielded four bands (R_f): green-yellow (0.80), brown-yellow (0.69), yellow-brown (0.45), and light brown (0.23). The light brown band was identified and characterized as $(\mu\text{-}H)_2(\eta^5\text{-}C_5H_5)IrOs_3(CO)_{10}$ (46.6 mg, 0.0420 mmol, 21% yield based on $(\mu\text{-}H)_2Os_3(CO)_{10}$) by the following methods. IR spectrum (cyclohexane, ν(CO)): 2091m, 2070m, 2044vs, 2004vs, 1992m(sh), 1974m, 1965m, 1824w cm^{-1}. ^{1}H NMR spectrum (CD_2Cl_2, −60°C): δ 5.8 (s, 5H), −18.95 (s, 1H), −21.28 (s, 1H) ppm. ^{13}C NMR spectrum (CD_2Cl_2, −60°C): 195.8 (s, 1C), 181.2 (s, 1C), 178.7 (s, 1C), 175.2 (s, 1C) 172.0 (d, J(CH) = 10.2 Hz, 1C), 169.9 (s, 1C), 168.1 (s, 1C), 167.2 (d, J(CH) = 10.4 Hz, 1C), 165.3 (d, J(CH) = 10.1 Hz, 1C), 164.3 (d, J(CH) = 11.4 Hz, 1C), 82.7 (s, 5C) ppm.

The other three fractions were characterized by ^{1}H NMR spectroscopy. First band, green-yellow (0.80), ^{1}H NMR spectrum ($CDCl_3$, 30°C): 5.82 (s), 5.63 (s), −15.75 (s), −17.84 (s), −20.47 (d, J(CH) = 5 Hz), −21.61 (s) ppm. Second band, brown-yellow (0.69), ^{1}H NMR spectrum ($CDCl_3$, 30°C): 5.50 (s), 5.37 (s), 4.77 (s),

Table 3

Selected bond distances (Å) and e.s.d.s for $(\mu\text{-}H)_2(\eta^5\text{-}C_5H_5)IrOs_3(CO)_{10}$

A. *Metal – metal distances*			
Os(1)–Os(2)	2.944(1)	Os(1)–Ir	2.749(1)
Os(1)–Os(3)	2.889(1)	Os(2)–Ir	2.798(1)
Os(2)–Os(3)	2.763(1)	Os(3)–Ir	2.740(1)
B. *Metal – carbonyl distances*			
Os(1)–C(11)	1.91(2)	Os(3)–C(31)	1.89(2)
Os(1)–C(12)	1.96(2)	Os(3)–C(32)	1.93(2)
Os(1)–C(13)	1.91(2)	Os(3)–C(33)	1.86(2)
Os(2)–C(21)	1.89(2)		
Os(2)–C(22)	1.94(2)	Os(2)–C(24)	2.38(2)
Os(2)–C(23)	1.93(2)	Ir–C(24)	1.90(2)
C. *Carbon – oxygen distances*			
C(11)–O(11)	1.12(2)	C(23)–O(23)	1.09(2)
C(12)–O(12)	1.06(2)	C(24)–O(24)	1.15(2)
C(13)–O(13)	1.14(2)	C(31)–O(31)	1.16(2)
C(21)–O(21)	1.14(2)	C(32)–O(32)	1.08(2)
C(22)–O(22)	1.11(2)	C(33)–O(33)	1.13(2)
D. *Metal – carbon and carbon – carbon ring distances*			
Ir–C(41)	2.28(2)	C(41)–C(42)	1.46(3)
Ir–C(42)	2.21(2)	C(41)–C(45)	1.35(3)
Ir–C(43)	2.22(2)	C(42)–C(43)	1.45(3)
Ir–C(44)	2.21(2)	C(43)–C(44)	1.43(3)
Ir–C(45)	2.24(2)	C(44)–C(45)	1.40(3)

3.86 (s), 3.40 (s), -19.9 (s) ppm. Third band, yellow-brown, ^{1}H NMR spectrum ($CDCl_2$, 30°C): 5.39 (s), 5.40 (m), -12.79 (dd, $J(CH) = 10$ Hz), -14.50 (s), -17.15 (s) ppm. Each of these bands appear to be mixtures present in insufficient quantities to be further separated, characterized, and identified.

Table 4

Selected bond angles (deg) and e.s.d.s for $(\mu\text{-H})_2(\eta^5\text{-}C_5H_5)IrOs_3(CO)_{10}$

A. *Intermetallic angles*			
Os(2)–Os(1)–Os(3)	56.53(2)	Os(1)–Os(3)–Os(2)	62.76(2)
Os(2)–Os(1)–Ir	58.74(2)	Os(1)–Os(3)–Ir	58.41(2)
Os(3)–Os(1)–Ir	58.08(2)	Os(2)–Os(3)–Ir	61.13(2)
Os(1)–Os(2)–Os(3)	60.71(2)	Os(1)–Ir–Os(2)	64.11(2)
Os(1)–Os(2)–Ir	57.14(2)	Os(1)–Ir–Os(3)	63.50(2)
Os(3)–Os(2)–Ir	59.03(2)	Os(2)–Ir–Os(3)	59.84(2)
B. *Metal – metal – carbon angles*			
Os(2)–Os(1)–C(11)	100.0(7)	Os(1)–Os(2)–C(23)	102.4(7)
Os(3)–Os(1)–C(11)	146.7(7)	Os(3)–Os(2)–C(23)	81.7(6)
Ir–Os(1)–C(11)	90.2(7)	Ir–Os(2)–C(23)	140.6(6)
Os(2)–Os(1)–C(12)	145.9(6)	Os(1)–Os(3)–C(31)	101.2(6)
Os(3)–Os(1)–C(12)	97.3(5)	Os(2)–Os(3)–C(31)	158.9(6)
Ir–Os(1)–C(12)	89.8(7)	Ir–Os(3)–C(31)	99.3(5)
Os(2)–Os(1)–C(13)	113.8(6)	Os(1)–Os(3)–C(32)	144.8(6)
Os(3)–Os(1)–C(13)	117.6(5)	Os(2)–Os(3)–C(32)	92.9(6)
Ir–Os(1)–C(13)	173.5(6)	Ir–Os(3)–C(32)	88.2(6)
Os(1)–Os(2)–C(21)	152.2(6)	Os(1)–Os(3)–C(33)	116.7(6)
Os(3)–Os(2)–C(21)	98.5(7)	Os(2)–Os(3)–C(33)	104.8(6)
Ir–Os(2)–C(21)	97.1(6)	Ir–Os(3)–C(33)	165.9(6)
Os(1)–Os(2)–C(22)	108.1(4)	Os(1)–Ir–C(24)	83.2(8)
Os(3)–Os(2)–C(22)	168.3(4)	Os(2)–Ir–C(24)	57.2(7)
Ir–Os(2)–C(22)	119.4(5)	Os(3)–Ir–C(24)	116.6(7)
C. *Carbon – metal – carbon angles*			
C(12)–Os(1)–C(11)	92.2(8)	C(32)–Os(3)–C(31)	94.4(8)
C(13)–Os(1)–C(11)	92.6(9)	C(33)–Os(3)–C(31)	94.6(8)
C(13)–Os(1)–C(12)	97.1(9)	C(33)–Os(3)–C(32)	92.9(8)
C(22)–Os(2)–C(21)	93.2(8)	C(24)–Os(2)–C(21)	96.8(8)
C(23)–Os(2)–C(21)	91.6(9)	C(24)–Os(2)–C(22)	77.5(7)
C(23)–Os(2)–C(22)	98.3(8)	C(24)–Os(2)–C(23)	170.8(9)
D. *Metal – carbon – metal angles*			
Ir–C(24)–Os(2)	80.8(7)		
E. *Metal – carbon – oxygen angles*			
Os(1)–C(11)–O(11)	175.0(2)	Os(2)–C(24)–O(24)	127.0(2)
Os(1)–C(12)–O(12)	176.0(2)	Os(3)–C(31)–O(31)	177.0(2)
Os(1)–C(13)–O(13)	177.0(2)	Os(3)–C(32)–O(32)	178.0(2)
Os(2)–C(21)–O(21)	178.0(2)	Os(3)–C(33)–O(33)	176.0(2)
Os(2)–C(22)–O(22)	174.0(2)	Ir–C(24)–O(24)	148.0(2)
Os(2)–C(23)–O(23)	176.0(2)		
F. *Carbon angles within ring*			
C(45)–C(41)–C(42)	108.0(2)	C(43)–C(44)–C(45)	109.0(2)
C(41)–C(42)–C(43)	107.0(2)	C(44)–C(45)–C(41)	111.0(2)
C(42)–C(43)–C(44)	105.0(2)		

Results and discussion

$(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{IrOs}_3(\text{CO})_{10}$, an air stable, orange-red solid, was prepared in 21% yield according to the following reaction.

$$(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10} + (\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})_2 \xrightarrow[90°\text{C}]{\text{toluene}} (\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{IrOs}_3(\text{CO})_{10} \quad (1)$$

It was characterized by IR, ^{1}H and ^{13}C NMR, and mass spectrometry, and by single crystal X-ray crystallography. Selected distances and angles are given in Tables 3 and 4. The molecular structure of $(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{IrOs}_3(\text{CO})_{10}$ (Fig. 1) is similar to the structures of $(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{CoOs}_3(\text{CO})_{10}$ [2] and $(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{RhOs}_3(\text{CO})_{10}$ [5,7]. A semi-bridging carbonyl group resides across the Ir–Os(2) bond. Although the hydride ligands were not located, their presence across the Os(1)–Os(2) and Os(1)–Os(3) atoms is inferred from criteria established by Churchill [18]. Hydrogen bridged and non-bridged osmium–osmium bond distances agree well with those in $(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{CoOs}_3(\text{CO})_{10}$ [2] (2.940(1), 2.870(1), 2.778(1) Å) and $(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{RhOs}_3(\text{CO})_{10}$ [5,7] (2.950(1), 2.867(1), 2.782(1) Å) and fall within the range observed for comparable bonds in other neutral tetrahedral osmium containing clusters [19–22].

The bridging character of the semi-bridging carbonyl increases as M = Ir < Rh < Co. With increased tendency of the carbonyl to bridge the M–Os bond, the M–Os distance decreases relative to the non-bridged M–Os bond distances: Ir–Os

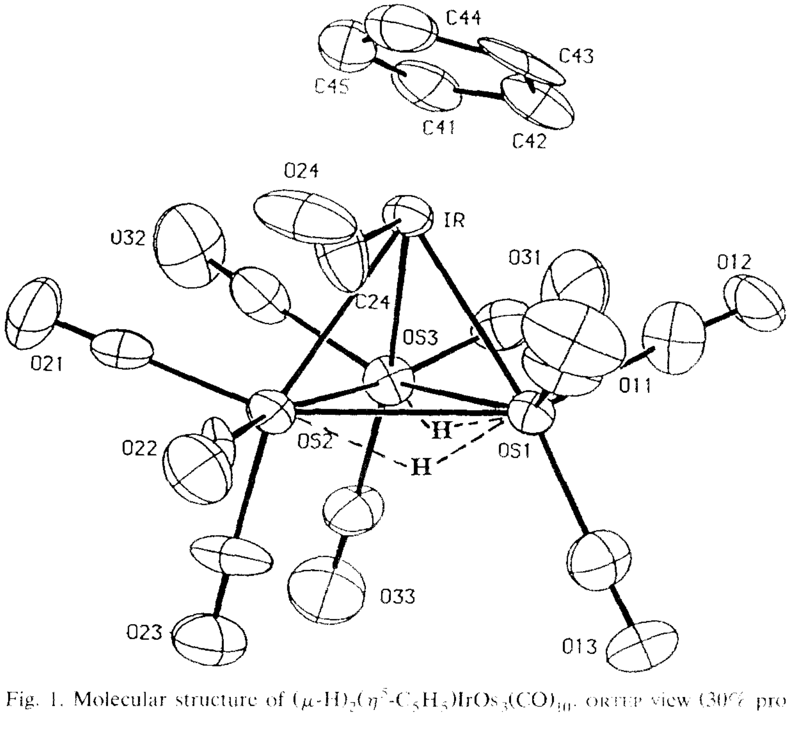
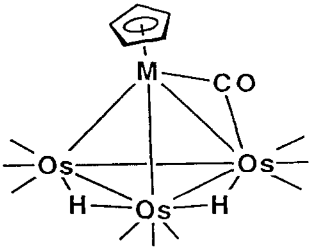


Fig. 1. Molecular structure of $(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{IrOs}_3(\text{CO})_{10}$. ORTEP view (30% probability ellipsoids).



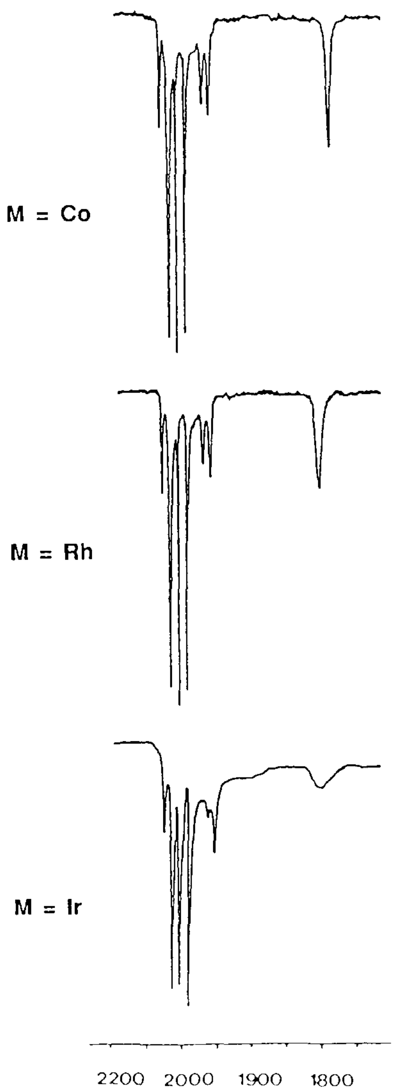


Fig. 2. Infrared spectra (hexanes, ν(CO)) of $(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{MOs}_3(\text{CO})_{10}$ (M = Co, Rh, Ir).

bridged distance = 2.798(1) Å, Ir–Os non-bridged distances = 2.749(1) Å and 2.740(1) Å; Rh–Os bridged distance = 2.736(1) Å; Rh–Os non-bridged distances = 2.730(1) Å and 2.729(1) Å; Co–Os bridged distance = 2.645(1) Å, Co–Os non-bridged distance = 2.672(1) Å and 2.680(1) Å. The semi-bridging Co–Os bond is the shortest Co–Os bond, while the semi-bridging Ir–Os bond is the longest Ir–Os bond. Increasing semi-bridging character leads to longer $\text{Os–C}_{\text{bridge}}$ bond distances in the series proceeding from cobalt to iridium, 2.208(1) Å, 2.231 Å, and 2.38(2) Å, respectively.

Figure 2 gives the IR spectra of $(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{CoOs}_3(\text{CO})_{10}$ [2], $(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{CpRhOs}_3(\text{CO})_{10}$ [5,7], and $(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{IrOs}_3(\text{CO})_{10}$. The intensity of the bridge carbonyl stretching band of $(\mu\text{-H})_2(\eta^5\text{-C}_5\text{H}_5)\text{IrOs}_3(\text{CO})_{10}$ is less than

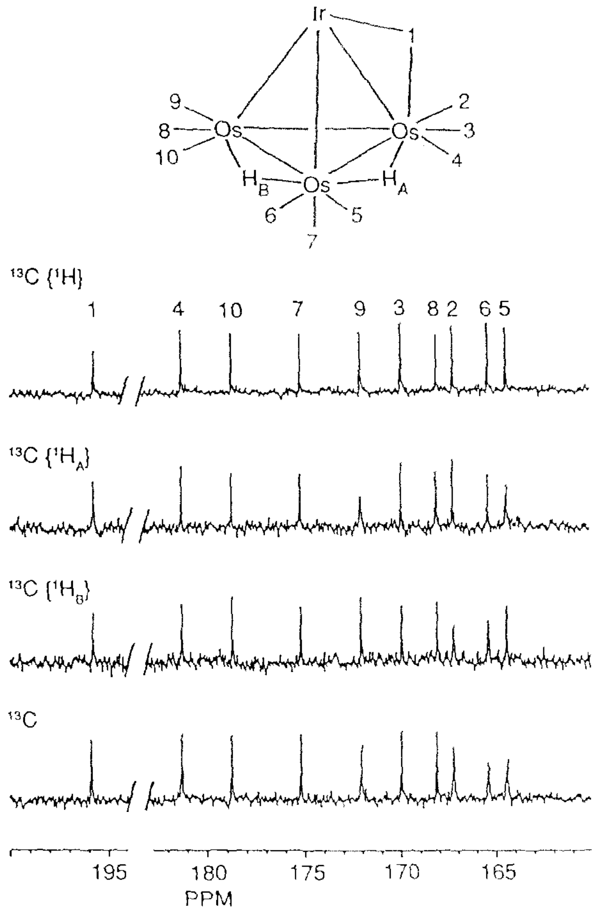


Fig. 3. ^{13}C NMR spectra (CD_2Cl_2, −60°C) of the carbonyl carbons of $(\mu\text{-}H)_2(\eta^5\text{-}C_5H_5)IrOs_3(CO)_{10}$.

and is broadened compared to the corresponding bands of the $CoOs_3$ and $RhOs_3$ clusters.

The ^{13}C NMR spectrum of $(\mu\text{-}H)_2(\eta^5\text{-}C_5H_5)IrOs_3(CO)_{10}$ at room temperature consists of a sharp singlet at 194 ppm and a broad indistinct signal at ~ 160 ppm, indicative of rapid exchange of the terminal carbonyls. The $(\eta^5\text{-}C_5H_5)$ resonance is a sharp singlet at 83.1 ppm. At low temperature ten distinct carbonyl signals appear in the ^{13}C NMR spectrum (Fig. 3). Table 5 lists the ^{13}C NMR signals for the carbonyl carbons at −60°C. The singlet at 195.8 ppm is assigned to the semi-bridging carbonyl (1). It occurs at higher field than the corresponding signals from the $CoOs_3$ [2] and $RhOs_3$ [5,7] clusters (237.4 and 222.3 ppm respectively), consistent with the trend of semi-bridging nature of the carbonyl in this series of clusters. Carbonyls (2,6) are *trans* to H_A and (5,9) are *trans* to H_B. Comparison of the ^1H decoupled spectrum with selectively decoupled H_A and H_B spectra permits the assignments: H_A *cis* to carbonyl 5, H_B is *cis* to carbonyl 6. Carbonyl 5 exhibits *cis* coupling ($J(CH) = 1.2$ Hz) to H_A when it is decoupled from H_B and the assignment of carbonyl 6 is based on comparison of the intensities of the selectively

Table 5

^{13}C NMR data (300 MHz) for $(\mu\text{-}H)_2(\eta^5\text{-}C_5H_5)IrOs_3(CO)_{10}$ in CH_2Cl_2 at $-60°C$

δ (ppm)	Assignment (see Fig. 3)
195.8 (s)	1
181.2 (s)	4
178.7 (s)	10
175.2 (s)	7
172.0 (d, $J(CH) = 10.2$ Hz)	9
169.9 (s)	3
168.1 (s)	8
167.2 (d, $J(CH) = 10.4$ Hz)	2
165.3 (d, $J(CH) = 10.1$ Hz)	6
164.3 (d, $J(CH) = 10.4$ Hz)	5

decoupled spectra. Assignments of remaining carbonyls were made in a similar manner. Lower field terminal carbonyl signals are assigned to carbonyls 4, 10, and 7 since axial carbonyls generally have resonances at lower field than radial carbonyls [25]. Specific assignments are based on comparisons of intensities of the coupled and decoupled spectra. The remaining carbonyls are assigned in a similar fashion. Variable temperature ^{13}C NMR spectra of the cluster were obtained between -80 and 30°C. Except for the signal assigned to carbonyl 10, the signals for the terminal carbonyls broaden and collapse into the baseline at -25°C. At -20°C the only visible signal in the low field ^{13}C NMR spectrum is that assigned to the bridging carbonyl, 1. These results indicate that except for carbonyl 10, the terminal carbonyls all participate in the initial exchange process, which eventually does incorporate carbonyl 10. The bridging carbonyl, 1, does not participate in the exchange, even at 30°C.

The ^1H NMR spectrum at room temperature consists of a sharp peak at 5.80 ppm assigned to the $(\eta^5\text{-}C_5H_5)$ group and a very broad peak centered at -20.0 ppm indicating the fluxional nature of the hydrides. At -60°C two bridging hydride peaks appear at -18.95 and -21.29 ppm for H_B and H_A (Fig. 3) respectively. Assignments are based on related compounds [1,4,5]; osmium–osmium bridging hydrogens *cis* to a carbonyl bridge have NMR chemical shifts at higher field than -20 ppm and osmium–osmium bridging hydrogens not *cis* to a bridging carbonyl have NMR chemical shifts at lower field than -20 ppm [20,24].

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Supplementary material. A complete list of crystal data, positional parameters, anisotropic thermal parameters, bond distances, and bond angles and a table of calculated and observed structure factor amplitudes is available upon request from the National Auxiliary Publications Service (NAPS). See NAPS document no. 04905 for 31 pages of supplementary material. Order from NAPS, c/o Microfiche Publications, P.O. Box 3515, Grand Central Station, New York, NY 10163-3513. Remit with your order, not under separate cover, \$11.05 (US funds on a US Bank only) for photocopies or \$4.50 for microfiche. Outside the United States and Canada add postage of \$4.50 for the first 20 pages and \$1.00 for each additional 10 pages of material thereafter, \$1.75 for microfiche postage. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15.00, plus applicable postage.

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